Midterm Exam **Soft Condensed Matter Theory**, April 20, 2016, 13:30h-16:30.
This exam consists of 20 items divided into 4 problems. The maximum score for each item is 5 points. Write your name on each page. This is a *closed-book* exam, and electronic tools are **not** allowed.

Problem 1

Consider a single colloidal particle of mass m and charge q in a liquid at room temperature T in which a homogeneous static electric field exists with x-component E. We only consider the position $x(t)$ and the velocity $v(t)$ along the Cartesian x-direction at time t. Ignoring fluctuations, the Langevin equation with friction coefficient $\xi > 0$ takes the form

$$\frac{dv(t)}{dt} = -\xi v(t) + m^{-1} qE. \tag{1}$$

(a) Solve this equation, for $t > 0$, for the case that $x(0) = 0$ and $v(0) = 0$.

(b) If the density of colloids is ρ and the system is in a stationary state, give an expression for the conductivity σ defined by $j = \sigma E$ with j the charge flux (in the x-direction).

The external field is now switched to zero, $E = 0$, such that the only force on a single colloid is the friction force and a fluctuating force $f(t)$ that for all $s, s' \geq 0$ satisfies $\langle f(s) \rangle = 0$ and $\langle v(0) f(s) \rangle = 0$, with a white-noise character given by $\langle f(s) f(s') \rangle = 2mk_B T \xi \delta(s - s')$. The brackets $\langle \cdots \rangle$ denote an average over many trajectories.

(c) Describe the origin of this fluctuating force in a few words and comment on the exactness and/or the approximation that underly the white-noise character.

(d) Give the corresponding Langevin equation and show that its solution is $v(t) = v_0 \exp(-\xi t) + \exp(-\xi t) m^{-1} \int_0^t f(s) \exp(\xi s) ds$ with $v_0 = v(0)$ the initial velocity.

(e) Calculate the mean-square x-displacement $\langle x^2(t) \rangle$ for $t \gg \xi^{-1}$.

Problem 2

Consider an isotropic and homogeneous fluid of N identical particles with mass m, momenta $\mathbf{p}_i$ and positions $\mathbf{r}_i$ for $i = 1, \cdots, N$, in a volume V at temperature T. The Hamiltonian reads $H(\Gamma) = K + \Phi$ with $K = \frac{1}{2m} \sum_{i=1}^N \mathbf{p}_i^2$ and $\Phi = \sum_{i<j}^N \phi(r_{ij})$ with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\phi(r)$ the pair potential, where $\Gamma = (\mathbf{p}_1, \cdots, \mathbf{r}_N)$ denotes the microscopic state in $6N$-dimensional phase space. The canonical partition function is
$Z(N, V, T) = (N! h^{3N})^{-1} \int d\Gamma \exp(-\beta H(\Gamma))$, with $\beta^{-1} = k_B T$ and h the Planck constant. The density is $\rho = N/V$, the ensemble average is denoted by $\langle \cdots \rangle$, and the pair-distribution function is defined as $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \langle \sum_{i \neq j}^N \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') \rangle$.

(a) Show that $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp[-\beta \Phi(\mathbf{r}_1, \cdots, \mathbf{r}_N)]/Q$ and define the normalization factor Q.

(b) Give arguments as to why one can write $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho^2 g(|\mathbf{r} - \mathbf{r}'|)$ with $g(r)$ the radial distribution function, and show for arbitrary $\phi(r)$ that $\langle H \rangle = \frac{3}{2} N k_B T + \frac{1}{2} V \rho^2 \int d\mathbf{r} g(r) \phi(r)$.

(c) Sketch $g(r)$ of a hard-sphere fluid (diameter σ) for packing fractions (i) $\eta = 0.001$ and (ii) $\eta = 0.5$. Think of units on the axes. Also calculate the second-virial coefficient of this system.

Consider a gas-liquid interface with surface tension γ and mass density difference $\Delta\rho$ between the bulk liquid and bulk gas phase, in the Earth's gravity field with acceleration g pointing in the negative z-direction. Denoting the horizontal position by (x, y) and the local height of the interface by $z = h(x, y)$ (so we ignore overhangs), with $\int dxdyh(x, y) = 0$, we can write for the capillary-wave Hamiltonian $H_{cw} = (\gamma/2)\int dxdy[(\partial_x h)^2 + (\partial_y h)^2 + h^2/\ell^2]$.

(d) Explain the physics behind the terms in H_{cw} and derive an expression for the capillary length ℓ.

(e) Diagonalize H_{cw} by a Fourier analysis, and explain *how* the roughness $\langle\int dxdyh^2(x, y)\rangle$ can be calculated from the Fourier representation.

Problem 3 Consider a bulk one-component fluid of density $\rho = N/V$ at temperatute T of which the pressure is given by $p(\rho, T) = k_B T(\rho + \frac{b}{2}\rho^2 + \frac{c^2}{3}\rho^3)$ with $b(T) = 3(T/T^* - 1)c$, with T^* and c positive known constants. The Debroglie wavelength of the particles is Λ.

(a) Give a physical interpretation of c and sketch a pair potential that could give rise to $b(T)$.

(b) Calculate the critical temperature T_c and the critical density ρ_c of this fluid.

(c) Calculate the chemical potential $\mu(\rho, T)$ of this fluid.

(d) Describe in a few words the state of this fluid at $T = \frac{1}{2}T_c$ and $\rho = \rho_c$.

(e) Give the order of magnitude of the thickness of the vapour-liquid interface of Argon far below the critical temperature.

Problem 4

(a) Describe (i) whether or not a suspension of colloidal hard spheres can crystallise and (ii) how a gas-liquid transition can be induced in the fluid state of this system.

(b) Derive the Gibbs adsorption equation that relates the adsorption Γ on a planar substrate of areas A at temperature T to the surface tension γ and the chemical potential μ.

Consider a three-dimensional classical fluid with an isotropic pair potential $\phi(r)$ at chemical potential μ at temperature T in an external potential $V_{ext}(\mathbf{r})$. The intrinsic Helmholtz free energy functional is denoted by $\mathcal{F}[\rho]$, with $\rho(\mathbf{r})$ the one-body density as a function of the position $\mathbf{r}$.

(c) Give $\mathcal{F}[\rho]$ for the case that $\phi(r) \equiv 0$.

We now assume that the excess (non-ideal) part of $\mathcal{F}[\rho]$ is given by

$$\mathcal{F}_{exc}[\rho] = \frac{1}{2}k_B T\int d\mathbf{r}\int d\mathbf{r}'\rho(\mathbf{r})\rho(\mathbf{r}')f(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}\psi(\rho(\mathbf{r})), \tag{2}$$

with $f(\mathbf{r}, \mathbf{r}')$ the Mayer function and $\psi(\rho)$ a known function.

(d) Calculate the direct two-body correlation function $c^{(2)}(\mathbf{r}, \mathbf{r}')$.

(e) Give, as explicitly as possible, a condition for the equilibrium density profile $\rho_{eq}(\mathbf{r})$.

—THE END—